**Supporting Information**

# Measurements of isoprene-derived organosulfates in ambient aerosols by aerosol time-of-flight mass spectrometry- Part 1: Single particle atmospheric observations in Atlanta

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This supporting information contains 12 pages and 4 figures.

**Results & Discussion**

***Monoterpene-derived Organosulfates.*** Organosulfate species derived from monoterpenes have also been detected previously in the Atlanta region,[1] however, these species could not be unequivocally identified in the ATOFMS data. It is possible that the highly-branched and cyclic structure of these compounds make them more susceptible to fragmentation under laser desorption/ionization and thus were not detected as intact molecules that could be readily identified. Additionally, the ion transmission in the time-of-flight mass spectrometer utilized for these studies is significantly reduced at the high molecular weights characteristic of monoterpene-derived organosulfate species (> *m/z* 250). The reduced signal-to-noise ratio in this *m/z* range, combined with the mass calibration difficulties outlined in the Supporting Information of Part 2, likely prohibited the detection of monoterpene-derived organosulfates during AMIGAS. Additional characterization studies should be performed to assess the overall ATOFMS detection capabilities across the range of organosulfate compounds that have been detected in ambient aerosol particles.

***Trends in aerosol mixing state.*** It is also interesting to note from Figures 3 & 4 that the organosulfate species are found primarily on the carbonaceous aerosol types (e.g. organic carbon, elemental carbon/organic carbon) while the inorganic types (e.g. sea salt) are lacking organosulfates. There are several possible explanations for this observation. The mixing state dependence could indicate preferential partitioning of the organosulfate precursors into a carbonaceous particle matrix. It is also possible that the disparity in organosulfate content between organic and inorganic particle types is simply due to the size ranges characteristic of these particle types- the carbonaceous types typically dominate the submicron mode, while the inorganic types are generally detected in the supermicron mode. Therefore, organosulfates could be found predominantly on the carbonaceous particle types simply because they dominate the

size range with the highest surface-to-volume ratio as opposed to exhibiting more favorable gas-to-particle partitioning of organosulfate precursors. Also of note, previous ATOFMS studies have found that the acidity increases as particle size decreases,[2] consistent with the findings described in the main paper that the organosulfate-containing particles were more strongly enriched in sulfate.

***ATOFMS Particle Types.*** Average mass spectra for each particle type are shown in Figure S3a for particles containing organosulfates and Figure S3b for particles that did not contain organosulfates during AMIGAS and Figures S4a and S4b for ANARChE. Note that these mass spectra were averaged across particles with different mass calibrations. The particle types are assigned and named based on comparison between the mass spectral fingerprints and previously identified source libraries. A brief discussion of the key characteristics for each particle type is provided here for reference.

*Elemental Carbon (EC).* Elemental carbon particles display an intense series of carbon clusters ($^{12n}C_n$) in both positive and negative spectra. There were no EC particles that contained organosulfates during AMIGAS and 3125 (82%) that contained low levels during ANARChE.

*Elemental Carbon/Organic Carbon (ECOC).* This type is identified by the presence of small carbon clusters ($C_n$, n=1-3) mixed with less intense organic carbon fragments ($^{27}C_2H_3$, $^{43}C_2H_3O$) in the positive spectra. The negative spectra contain the secondary species, sulfate ($^{-97}HSO_4$) and nitrate ($^{-62}NO_3$, $^{-46}NO_2$). There were no ECOC particles detected that did not contain organosulfates during AMIGAS and 1067 (~3%) with undetectable amounts during ANARChE.

*Organic Carbon (OC).* OC is dominated by organic fragments in the positive spectra ($^{27}C_2H_3$, $^{39}C_3H_3$, $^{43}C_2H_3O$). The negative spectra contain primarily sulfate ($^{-97}HSO_4$) and nitrate ($^{-62}NO_3$, $^{-46}NO_2$). The OC particles that contained organosulfates (AMIGAS: 19892 particles, 96%;

ANARChE: 110912, >99%) were significantly more abundant than those lacking organosulfates (AMIGAS: 913 particles, 4%; ANARChE: 706, <0.01%).

*Amine.* The positive spectra of the amine-type are enriched in the organic-nitrogen markers, $^{58}C_2H_5NCH_2$, $^{86}(C_2H_5)_2NCH_2$, $^{101}(C_2H_5)_3N$ with less intense organic carbon ($^{27}C_2H_3$, $^{39}C_3H_3$, $^{43}C_2H_3O$) fragments. The negative spectra are characterized by a large sulfate ($^{-97}HSO_4$) contribution with smaller nitrate ($^{-62}NO_3$, $^{-46}NO_2$) peaks. All of the amine particles contained organosulfates during both studies likely due to the highly aged nature of these particles as indicated by the high abundance of secondary amine species.

*Biomass.* Particles attributed to biomass burning contain a dominant potassium ($^{39}K$) peak with smaller sodium ($^{23}Na$) and carbonaceous peaks ($^{12}C$, $^{27}C_2H_3$, $^{37}C_3H$) in the positive spectra. The negative spectra are primarily sulfate ($^{-97}HSO_4$) and nitrate ($^{-62}NO_3$, $^{-46}NO_2$). The biomass particles that contained organosulfates (AMIGAS: 4596 particles, 42%; ANARChE: 14505, 82%) were more strongly enriched in sulfate than those lacking organosulfates (AMIGAS: 6353 particles, 58%; ANARChE: 3248, 18%).

*Dust.* Dust particles are typified by the presence of minerals, such as sodium ($^{23}Na$), aluminum ($^{27}Al$), calcium ($^{40}Ca$), or iron ($^{56}Fe$). The negative spectra contain nitrate ($^{-62}NO_3$, $^{-46}NO_2$) and aluminosilicates ($^{-76}$ $AlO_2(OH)/SiO_3$). The positive and negative spectra included in Figure S5b are an average of multiple dust particle types. Only 208 (3%) iron-rich dust particles were found to contain organosulfates during AMIGAS.

*Sea Salt.* Sea salt contains primarily sodium ($^{23}Na$) with a smaller contribution from potassium/sodium oxide ($^{39}K/NaO$) in the positive spectra. Prominent negative ions include chloride ($^{-35,-37}Cl$), organonitrogen ($^{-26}CN$), sulfate ($^{-97}HSO_4$), and nitrate ($^{-62}NO_3$, $^{-46}NO_2$). Sea

salt was introduced to the inland Atlanta region during AMIGAS by the tropical cyclones.[3] No sea salt particles were detected that contained organosulfates.

*Ca-rich.* The Ca-rich particle type observed during ANARChE is characterized by an intense calcium ($^{40}Ca$) peak, with a smaller sodium ($^{23}Na$) peak in the positive spectra. The negative spectra contain sulfate ($^{-97}HSO_4$), and nitrate ($^{-62}NO_3$, $^{-46}NO_2$). In ANARChE, 261 (48%) particles were found to contain organosulfates, while 280 (52%) did not.

*Na-rich.* The Na-rich particle type identified in the ANARChE campaign contains strong sodium ($^{23}Na$) and potassium ($^{39}K$) peaks in the positive-ion spectra. This particle type is distinguished from sea salt due the presence of carbon ($^{12}C$) and the absence of chloride. The negative spectra contain sulfate ($^{-97}HSO_4$), and nitrate ($^{-62}NO_3$, $^{-46}NO_2$). During ANARChE, 1025 (34%) Na-rich particles were detected with organosulfates, while 1991 (66%) displayed undetectable organosulfate levels.

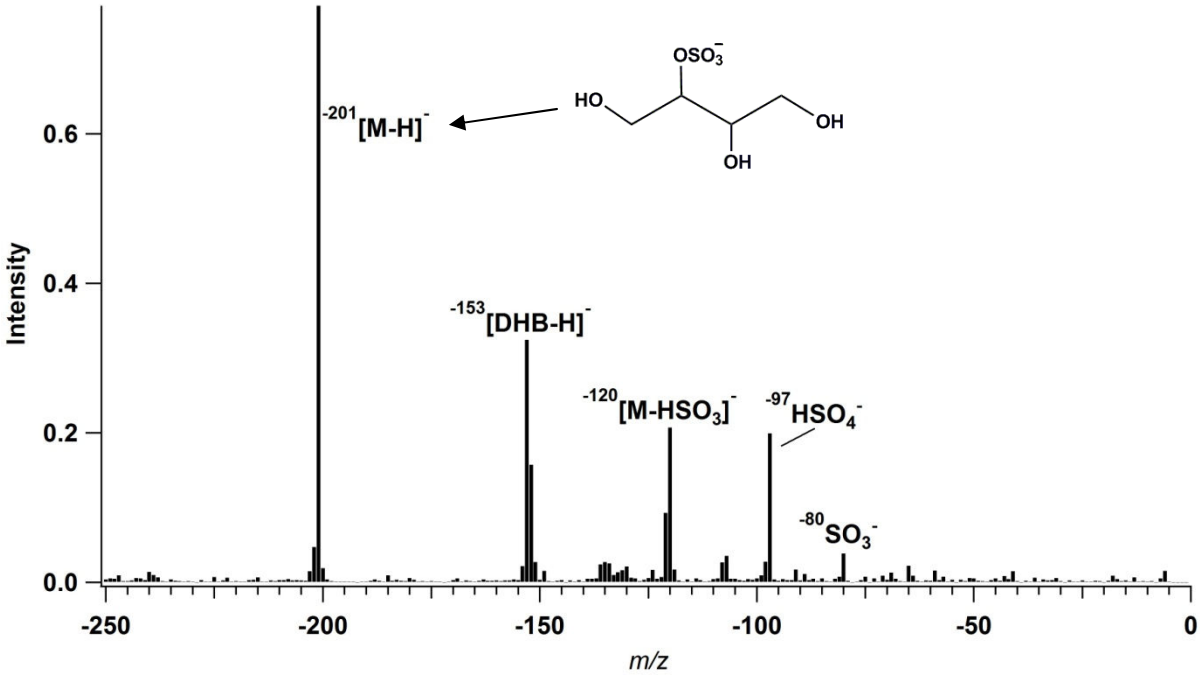


**Figure S1.** Average negative mass spectrum of a 2,3-epoxy-1,4-butanediol (BEPOX)-derived organosulfate standard. DHB is a matrix added to the standard solution.

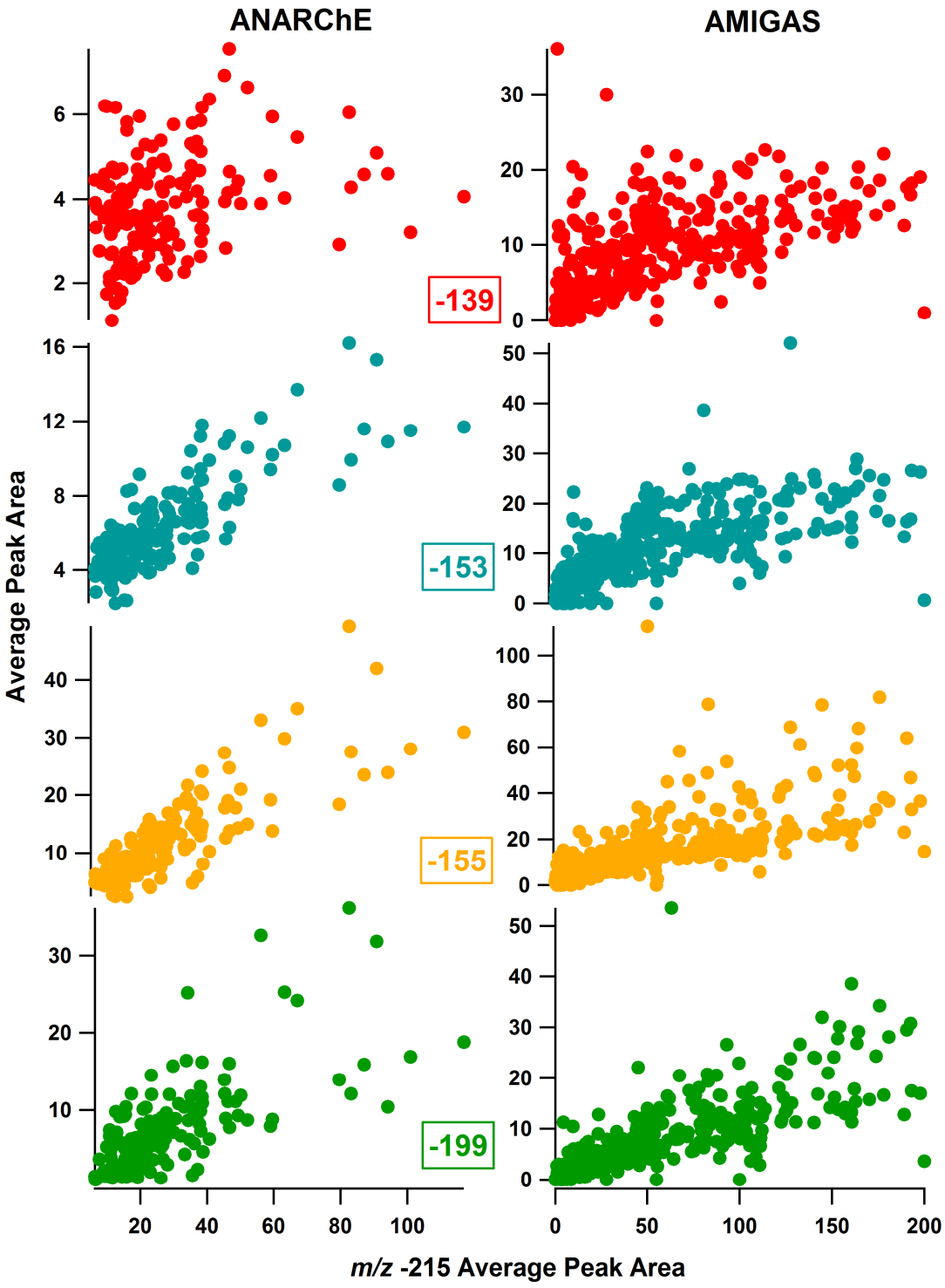


**Figure S2.** Correlations between the proposed organosulfate markers *m/z* -139, -153, -155, and -199 with *m/z* -215.

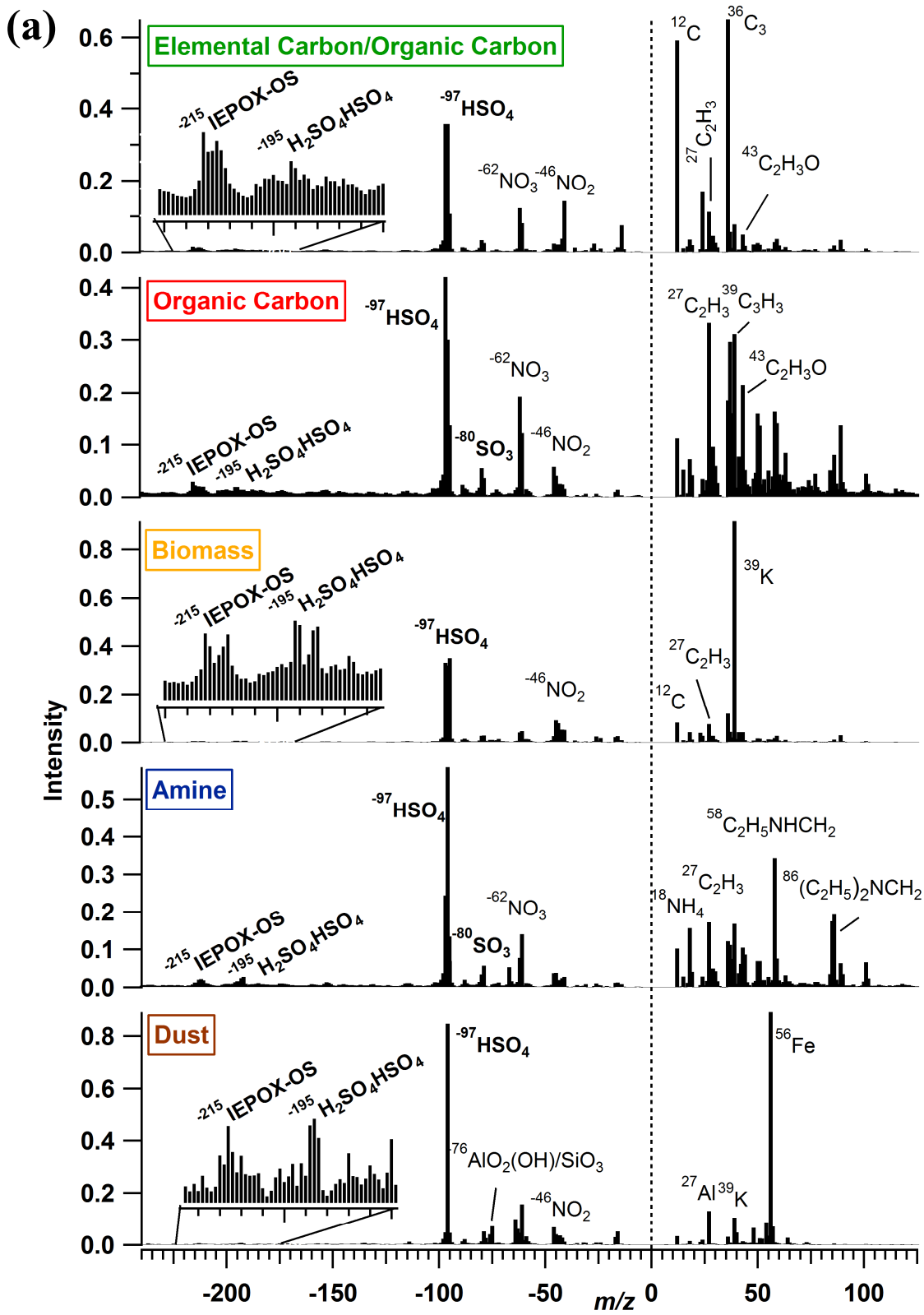


**Figure S3a**. Average mass spectra for the dominant particle types containing organosulfate species during AMIGAS.

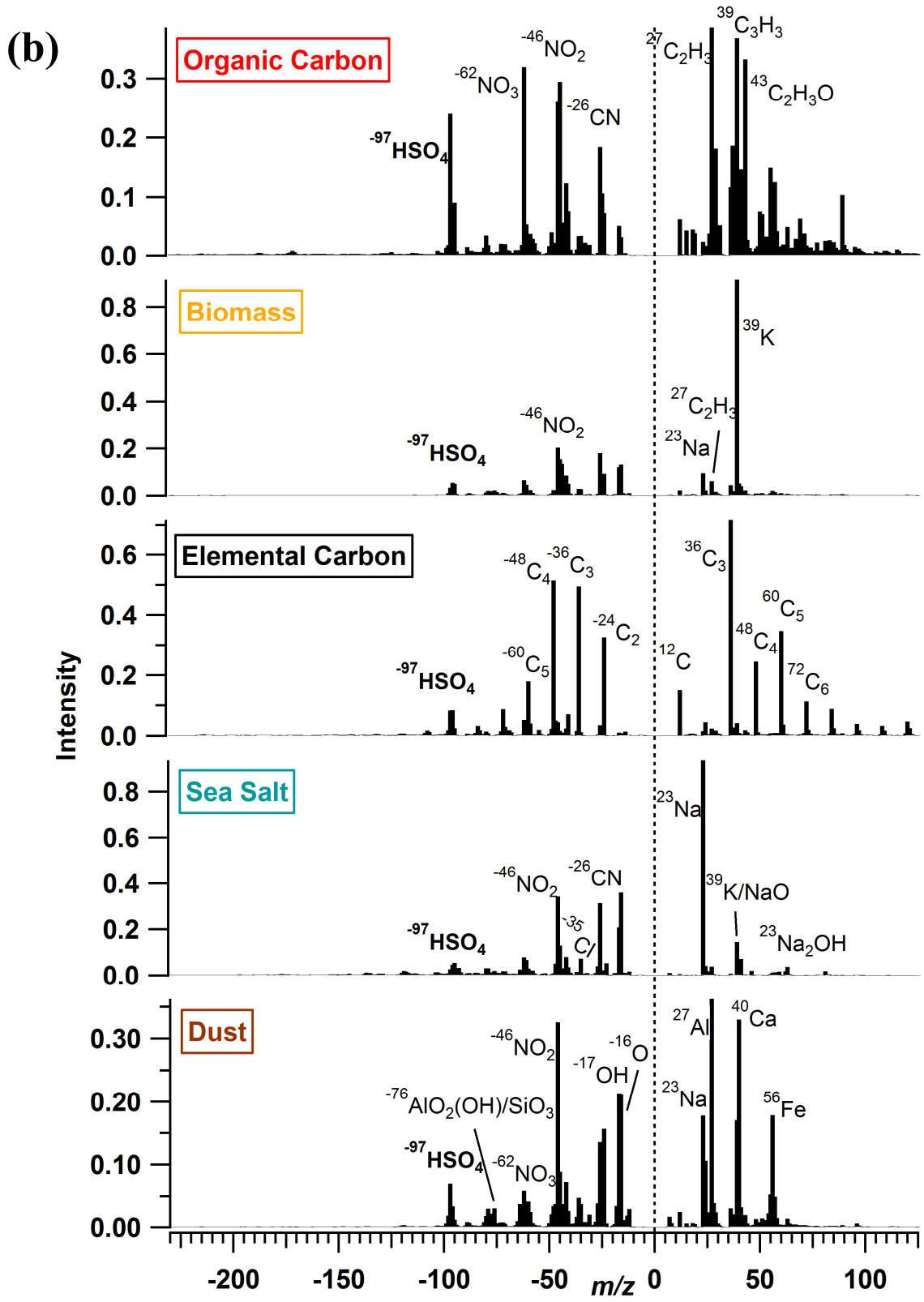


**Figure S3b.** Average mass spectra for the dominant particle types that did **not** contain organosulfate species during AMIGAS.

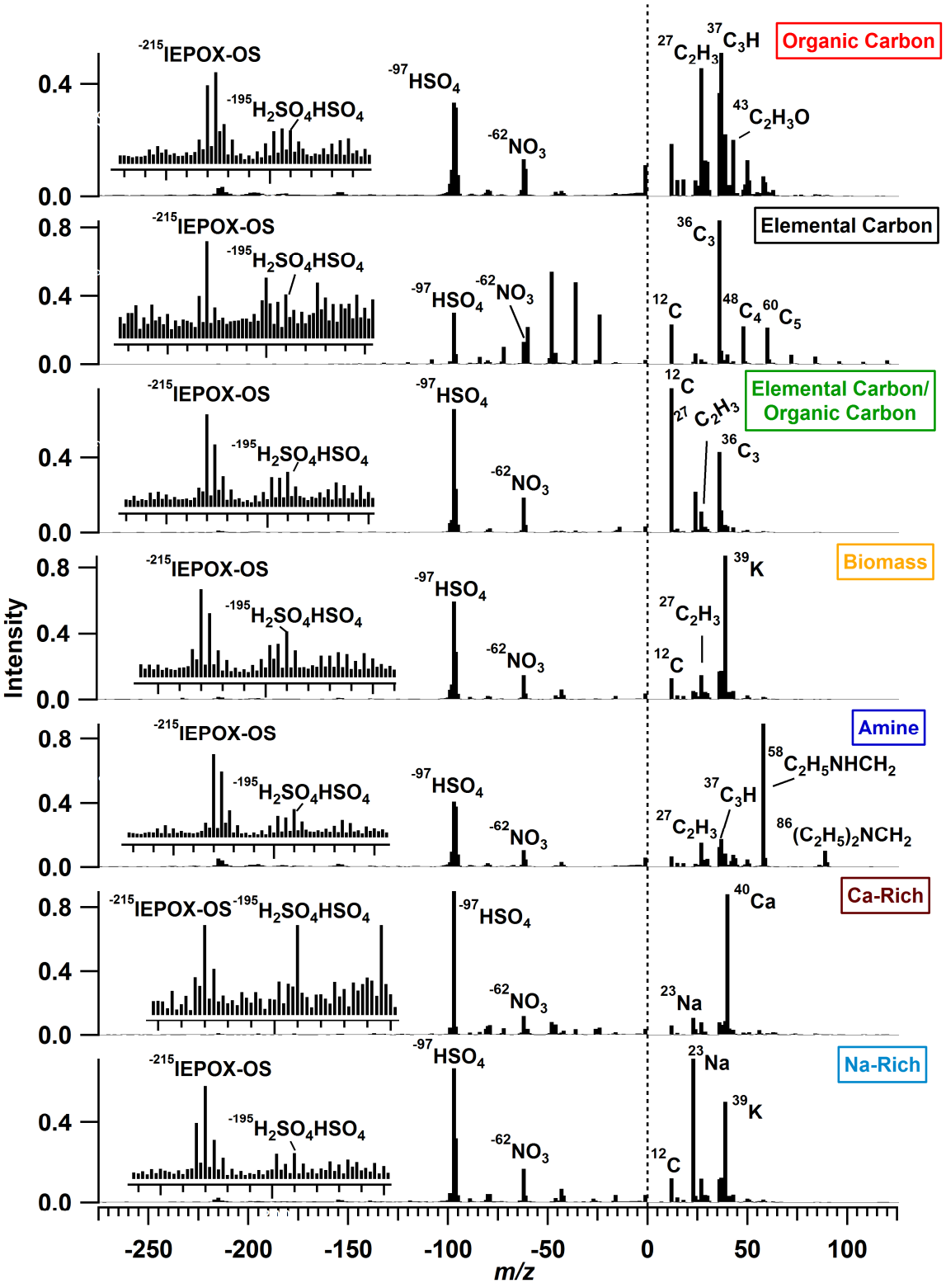


**Figure S4a**. Average mass spectra for the dominant particle types containing organosulfate species during ANARChE.

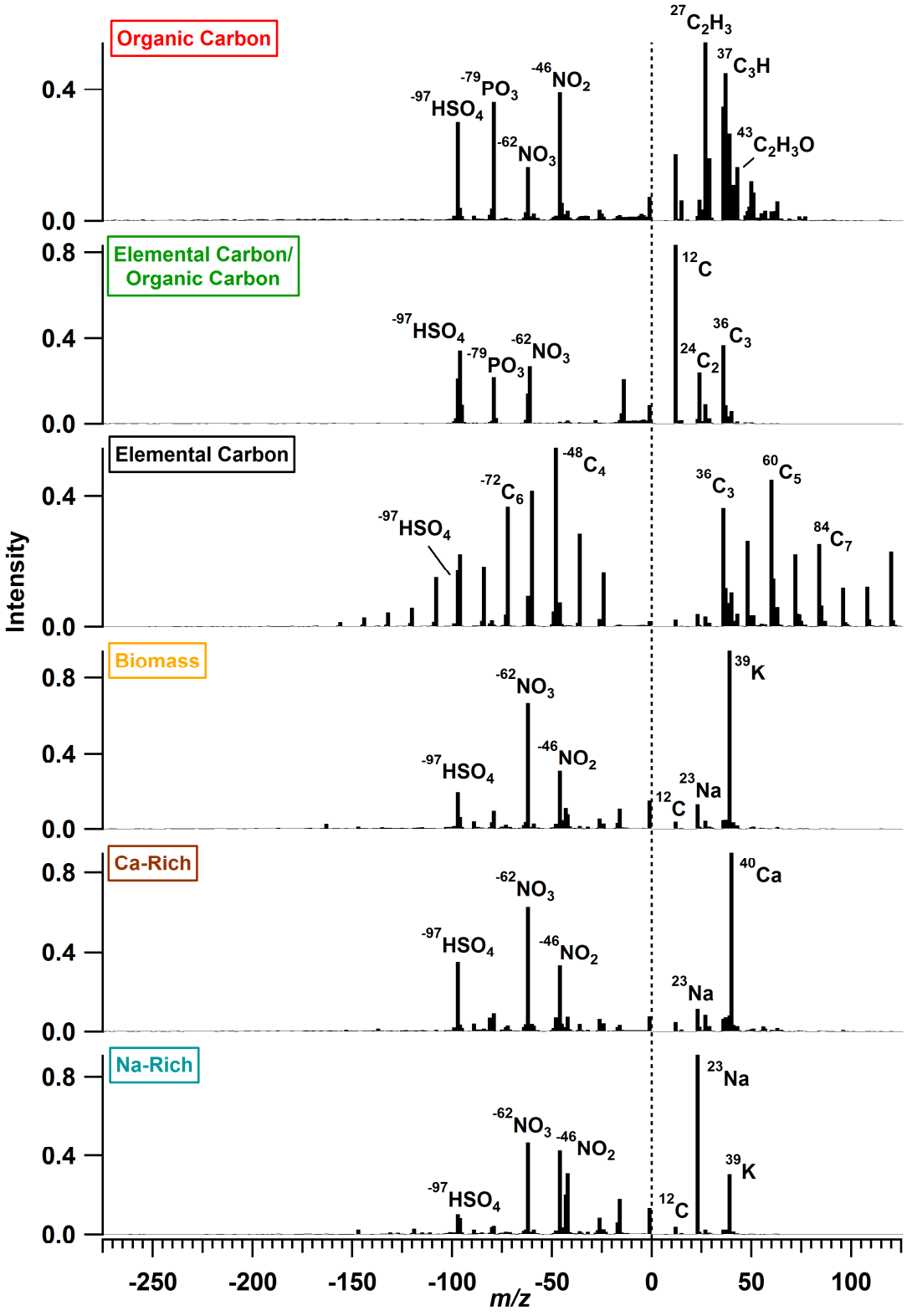


**Figure S4b.** Average mass spectra for the dominant particle types that did **not** contain organosulfate species during ANARChE.

**References**

1. Surratt, J. D.; Gómez-González, Y.; Chan, A. W. H.; Vermeylen, R.; Shahgholi, M.; Kleindienst, T. E.; Edney, E. O.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Maenhaut, W.; Claeys, M.; Flagan, R. C.; Seinfeld, J. H., Organosulfate formation in biogenic secondary organic aerosol. *J. Phys. Chem. A* **2008,** *112*, (36), 8345-8378.

2. Denkenberger, K. A.; Moffet, R. C.; Holecek, J. C.; Rebotier, T. P.; Prather, K. A., Real-time, single-particle measurements of oligomers in aged ambient aerosol particles. *Environ. Sci. Technol.* **2007,** *41*, (15), 5439-5446.

3. Creamean, J. M., Ault, A. P., Prather, K. A., Signature Marine Aerosol Chemistry Observed in an Inland Urban Location during Tropical Cyclones. *In preparation*.